

Formation of stratospheric nitric acid by a hydrated ion cluster reaction: Implications for the effect of energetic particle precipitation on the middle atmosphere

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[1] In order to improve our understanding of the effects of energetic particle precipitation on the middle atmosphere and in particular upon the nitrogen family and ozone, we have modeled the chemical and dynamical middle atmosphere response to the introduction of a chemical pathway that produces HNO_3 by conversion of N_2O_5 upon hydrated water clusters $\text{H}^+(\text{H}_2\text{O})_n$. We have used an ensemble of simulations with the National Center for Atmospheric Research (NCAR) Whole-Atmosphere Community Climate Model (WACCM) chemistry-climate model. The chemical pathway alters the internal partitioning of the NO_y family during winter months in both hemispheres, and ultimately triggers statistically significant changes in the climatological distributions of constituents including: i) a cold season production and loss of HNO_3 and N_2O_5 , respectively, and ii) a cold season decrease and increase in NO_x/NO_y -ratio and O_3 , respectively, in the polar regions of both hemispheres. We see an improved seasonal evolution of modeled HNO_3 compared to satellite observations from Microwave Limb Sounder (MLS), albeit not enough HNO_3 is produced at high altitudes. Through O_3 changes, both temperature and dynamics are affected, allowing for complex chemical-dynamical feedbacks beyond the cold season when the pathway is active. Hence, we also find a NO_x polar increase in spring-to-summer in the southern hemisphere, and in spring in the northern hemisphere. The springtime NO_x increase arises from anomalously strong poleward transport associated with a weaker polar vortex. We argue that the weakening of zonal-mean polar winds down to the lower stratosphere, which is statistically significant at the 0.90 level in spring months in the southern hemisphere, is caused by strengthened planetary waves induced by the middle and sub-polar latitude zonal asymmetries in O_3 and short-wave heating.

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1. Introduction

[2] Nitric acid (HNO_3) is considered to be a very important chemical species in the stratosphere. As a key reservoir for the reactive nitrogen (NO_x), HNO_3 intervenes in the nitrogen-dominated ozone (O_3) depleting cycle, and it plays an important role in the halogen-dominated catalytic cycle leading to polar O_3 depletion. For these reasons, the distribution of HNO_3 in the stratosphere has been studied closely with ground-based and satellite instruments. In the last two decades, a large amount of observations from several satellite-borne instruments, such as the Limb Infrared Monitor of the

Stratosphere Experiment (LIMS) on the NIMBUS 7, the Sub-Millimeter Radiometer (SMR) aboard Odin, the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) aboard ENVISAT, the Microwave Limb Sounder (MLS) aboard UARS and Aura, and the High Resolution Dynamics Limb Sounder (HIRDLS) also aboard Aura, has allowed the distribution of HNO_3 in the stratosphere to be characterized [Gille *et al.*, 1984; Santee *et al.*, 2004; Stiller *et al.*, 2005; Kinnison *et al.*, 2008; Orsolini *et al.*, 2009; Urban *et al.*, 2009].

[3] The primary chemical source of HNO_3 is the three-body gas-phase reaction between the hydroxyl radical (OH) and nitrogen dioxide (NO_2), while its major sinks are photolysis and oxidation by OH. While HNO_3 peaks in the winter lower stratosphere at high latitudes, enhanced abundances of HNO_3 are commonly observed in the polar mid and upper stratosphere, as revealed by ground-based [de Zafra *et al.*, 1997; McDonald *et al.*, 2000] and satellite observations [Austin *et al.*, 1986; Kawa *et al.*, 1995; Orsolini *et al.*, 2005; Stiller *et al.*, 2005; López-Puertas *et al.*, 2005;

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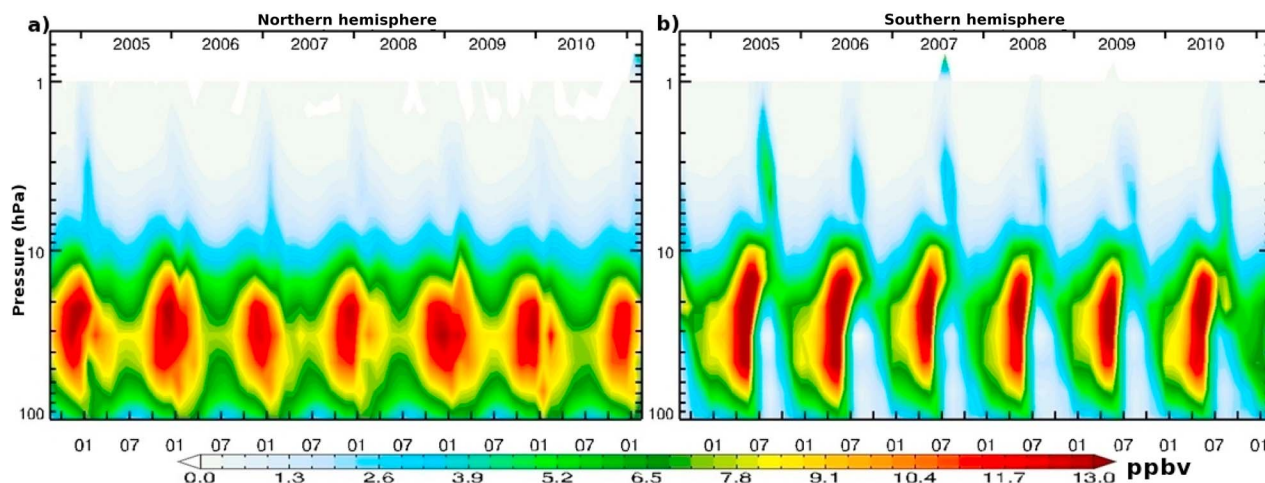


Figure 1. Time versus pressure evolution of HNO_3 (ppbv) averaged poleward of 70° in the (a) northern and (b) southern hemispheres, from August 2004 to February 2011, based on monthly means from MLS version 3.3. In this and in all following figures with time on the x axis, the tick marks indicate the middle of the month.

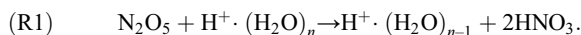
Orsolini *et al.*, 2009]. Figure 1 shows the monthly evolution of HNO_3 (averaged poleward of 70° in each hemisphere) observed by Aura/MLS (data version 3.3; see Appendix A) from August 2004 to February 2011. Descending tongues of HNO_3 -enriched air are apparent above 10 hPa during winter in both hemispheres above the main HNO_3 layer between approximately 100 and 10 hPa, which leads to a secondary maximum in the HNO_3 profile between 10 and 1 hPa.

[4] The intensity of these recurring HNO_3 enhancements between 10 and 1 hPa varies from year to year and appears stronger in the southern hemisphere (SH), where enhanced mixing ratios can reach approximately 6 ppbv. Up to the stratopause, the vertical extent of HNO_3 is comparable in both hemispheres. These MLS observations are in overall agreement with other instruments, as polar-averaged daily values ranging from 5 to 10 ppbv were reported between 25 and 40 km by SMR [Orsolini *et al.*, 2009] and MIPAS [Orsolini *et al.*, 2005; López-Puertas *et al.*, 2005]. Note that the early winter disappearance of the HNO_3 below about 30 hPa in the SH corresponds to the beginning of the polar stratospheric cloud (PSC) formation period, when uptake from the gas phase chemistry exists. In the northern hemisphere (NH) some discontinuities linked to stratospheric sudden warmings occur when the vortex undergoes weakening and displacement.

[5] Enhancement of mid and upper stratospheric HNO_3 is believed to be linked to a high-altitude source of NO_x . Energetic particle precipitation (EPP) can create NO_x in situ in the upper stratosphere during solar proton events (SPEs), via the so-called EPP/ NO_x “direct” effect [Jackman *et al.*, 2005, 2008; Randall *et al.*, 2006, 2009; Semeniuk *et al.*, 2011]. Upper-stratospheric NO_2 enhancements (above 100 ppbv) linked to EPP events have occasionally been observed [e.g., Callis and Lambeth, 1998; Orsolini *et al.*, 2005; López-Puertas *et al.*, 2005]. SPEs can induce a rapid HNO_3 enhancement lasting for a few days at altitudes of approximately 40 km and above, as observed during the strong SPEs of November 2001, October 2003 and January 2005 [Orsolini *et al.*, 2009; Verronen *et al.*, 2008, 2011].

Complex ion reactions have been proposed to foster these HNO_3 enhancements immediately following SPEs [Verronen *et al.*, 2008, 2011].

[6] Besides in situ stratospheric production, NO_x enhancements can arise from the descending flux of NO_x -rich air through the stratopause in the winter polar regions, the so-called EPP/ NO_x “indirect” effect. NO_x is produced in the mesosphere and thermosphere during the pervasive low energy auroral electron precipitation, or during more sporadic and higher energy electron precipitation events. Recurrent HNO_3 enhancements are associated with the EPP/ NO_x “indirect” effect; however, the production of NO_x as well as the efficiency of the mesosphere-to-stratosphere transport exhibits some variability, especially in the more dynamically active NH. Heterogeneous conversion of dinitrogen pentoxide (N_2O_5) to HNO_3 upon hydrated ion clusters [Böhlinger *et al.*, 1983; Kawa *et al.*, 1995] has been suggested as a probable explanation for the slower enhancements following the EPP/ NO_x “indirect” effect. In this case, the anomalously large NO_x concentration leads to excess N_2O_5 and then to the increased production of HNO_3 by conversion of N_2O_5 on hydrated water cluster ($\text{H}^+ \cdot (\text{H}_2\text{O})_n$):



[7] In the lower stratosphere, heterogeneous conversion of N_2O_5 on sulfate aerosols could also play a significant role in producing HNO_3 [e.g., Bekki *et al.*, 1997; de Zafra and Smyshlyaev, 2001].

[8] The high-altitude EPP-related source of HNO_3 is not well accounted for in stratospheric chemistry-transport models (CTM), or in middle atmosphere chemistry-climate models (CCM) as these models do not include the relevant ion chemistry. An exception to the former case is the recent study by Reddmann *et al.* [2010], who incorporated the ion cluster reaction (R1) into a chemistry-transport model. Focusing on the stratospheric NO_x and HNO_3 descent following the SPEs of October 2003, the HNO_3 abundance in

their model improved significantly with the inclusion of the afore mentioned reaction. Going beyond the study with prescribed stratospheric dynamics by *Reddmann et al.* [2010], in this paper we use a free-running CCM, which can produce coupled responses in both chemistry and dynamics. To this end, we use the Whole-Atmosphere Community Climate Model (WACCM) to investigate the role of reaction (R1) in the formation of HNO_3 enhancements through the NO_x indirect effect, and more generally its impact on the year-round evolution of stratospheric chemistry. We use an ensemble approach to study the primary chemical effects of the reaction as well as secondary effects due to combined, coupled changes in chemistry and dynamics. The model and the experimental setup are presented in Section 2, whereas the main results are presented in Section 3. Section 4 briefly addresses some of the biases in WACCM, and a discussion and a summary are provided in Section 5.

2. Modeling Methodology

2.1. Whole-Atmosphere Community Climate Model (WACCM)

[9] We use version 3.1.9 of WACCM developed at the National Center for Atmospheric Research (NCAR) [*Garcia et al.*, 2007]. WACCM covers the vertical region from the surface up to 6.0×10^{-6} hPa (equivalent to approximately 130 km geometric altitude) with 67 hybrid sigma-pressure levels. We have run WACCM with a horizontal resolution equivalent to $1.9^\circ \times 2.5^\circ$ (latitude \times longitude) and a time step of 1800 s for the physical parameterizations; this time step is further subdivided as necessary to ensure computational stability. WACCM incorporates a detailed neutral advection and chemistry model for the middle atmosphere, including heating due to chemical reactions; a model of ion chemistry in the mesosphere/lower thermosphere (MLT); ion drag and auroral processes; and parameterizations of shortwave heating at extreme ultraviolet wavelengths and infrared transfer under nonlocal thermodynamic equilibrium conditions. The WACCM chemistry module is derived from the three-dimensional chemical transport Model for Ozone And Related chemical Tracers version 3 (MOZART-3) described in *Brasseur et al.* [1998] and (<http://gctm.acd.ucar.edu/gctm/mozart>). It solves numerically 51 neutral species, including all the significant members of the O_x , NO_x , HO_x , ClO_x and BrO_x chemical families and respective reservoir species. Tropospheric source species such as N_2O , CH_4 , H_2O , chlorofluorocarbons (CFCs) and other halogenated compounds are included. Heterogeneous processes on sulfate aerosols and polar stratospheric clouds (liquid binary sulfate, supercooled ternary solutions, nitric acid trihydrate, and water ice), as well as aerosol sedimentation, are represented. The photolysis rates in WACCM for all absorbing species are calculated interactively. Further details regarding photolytic reaction rates and the chemistry module in general are given in *Kinnison et al.* [2007].

2.2. Model Setup

[10] To investigate the impact of HNO_3 formation by heterogeneous chemistry on hydrated ion clusters, we ran WACCM for 4 successive years. A simulation with an additional effective chemical reaction mimicking (R1) (“perturbed simulation” detailed below) is compared with a

control simulation without this reaction. Prescribed climatological sea surface temperatures were used, but the solar forcing and surface emissions correspond to the years 1998 to 2002. Since our aim is to model HNO_3 enhancements due to the EPP/NO_x “indirect” effect, individual SPEs are not introduced as forcing in our simulations. The diagnostics presented in this paper were carried out after a spin-up period of 6 months.

[11] Since WACCM is a free-running CCM, the inter-annual dynamical variability can be large. To minimize this internal variability, we used an ensemble approach in which we ran 4 pairs of 4-year control and perturbed simulations. This provides a total of 16 modeled years for each of the perturbed and control simulations. These 4 control and perturbed pairs (i.e., ensemble members) are initiated from different initial conditions, lagged by a day. Except in section 3.1, we only present ensemble-mean results with the statistical significance estimated by the standard Student t-test.

[12] Monthly mean distributions of minor species are interpreted with the aid of the Transformed Eulerian Mean (TEM) circulation. The total mass-weighted meridional circulation is calculated using monthly averaged dynamical fields. To represent the forcing of the TEM circulation by the resolved waves, we calculated the divergence of the Eliassen-Palm flux (EPFD), also using monthly averaged fields.

2.3. Additional HNO_3 Chemistry Introduced in WACCM

[13] The rate of the chemical reaction (R1) converting N_2O_5 to HNO_3 is controlled by the amount of N_2O_5 and $\text{H}^+(\text{H}_2\text{O})_n$ available. Following *de Zafra and Smyshlyaev* [2001], we treated the reaction as a pseudo first-order reaction with a rate constant $k_p = k_2(\text{H}^+(\text{H}_2\text{O})_n)$ where $k_2 = 3.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, yielding

$$\frac{d(\text{HNO}_3)}{dt} = -2 \frac{d(\text{N}_2\text{O}_5)}{dt} = 2k_p(\text{N}_2\text{O}_5).$$

[14] There is some uncertainty in the value of the k_2 constant. Based on *Böhrringer et al.* [1983], *de Zafra and Smyshlyaev* [2001] give a range of $8.0 \times 10^{-10} < k_2 < 4.0 \times 10^{-12}$. We used $k_2 = 3.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ near the upper limit, as suggested by *de Zafra and Smyshlyaev* [2001]. The reaction, in which one N_2O_5 molecule is lost and two HNO_3 molecules are produced, is processed in the implicit chemical solver for both species. The reaction has a side reaction consuming water vapor to regenerate the hydrated water cluster. However, this secondary effect was neglected here since it contributes as a marginal sink for stratospheric water vapor.

[15] We introduced a prescribed meridional distribution of hydrated water cluster $\text{H}^+(\text{H}_2\text{O})_n$ shown in Figure 2, corresponding approximately to the distribution shown in Figure 5a from *Beig et al.* [1993]. The prescribed time-independent distribution depends upon latitude and height, and is symmetrical around the equator. The densities peak near 4000 molec/cm^3 at polar latitudes and are tapered to zero at 30°N or S . Under normal conditions, galactic cosmic rays are the primary source of ions in the stratosphere. While varying with geomagnetic latitude and moderately influenced by the 11-year solar cycle and large magnetic storms,

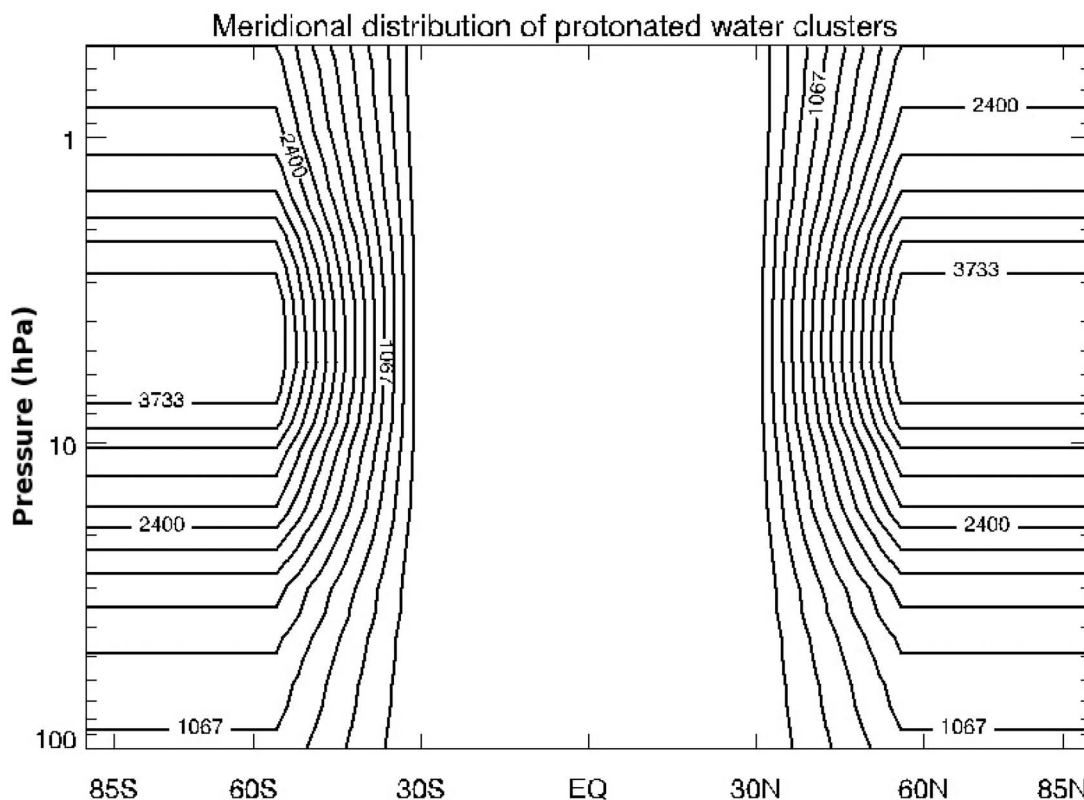


Figure 2. Prescribed meridional distribution of the density (molec/cm^3) of hydrated water cluster, $\text{H}^+(\text{H}_2\text{O})_n$, adapted from *Beig et al.* [1993].

the ion distribution exhibits relatively little short-term variation [de Zafra and Smyshlyaev, 2001]. As such, the use of a time-independent distribution of ion clusters serves as a good first order approximation.

3. Simulation Results

3.1. Primary Chemical Response in N_2O_5 and HNO_3

[16] Figure 3 shows the time evolution of differences in HNO_3 and N_2O_5 (averaged poleward of 70° in both hemispheres) between the perturbed and the control simulations over the pressure range 100–0.5 hPa. While we will display 4-member ensemble means in the rest of the paper, we show in Figure 3 the 4-yearlong simulation for a particular member to demonstrate the recurring conversion of N_2O_5 to HNO_3 in the mid-stratosphere in any given simulation. The corresponding distributions from the control simulation are also shown as dashed contour lines. A recurrent annual HNO_3 increase in the perturbed simulation appears when and where N_2O_5 is present. N_2O_5 is only abundant in the polar regions during the cold and dark season, i.e., during October to February in the NH, and April to August in the SH, when its thermal decomposition and photochemical conversion are slow. The magnitude of HNO_3 enhancements in the perturbed simulation are up to 6 ppbv near 20 hPa. In both hemispheres, the recurrent increase in HNO_3 in the perturbed simulation, around 30–10 hPa, is found above the maximum volume mixing ratio (vmr) in the control simulation. While the increase coincides in time with the winter maximum in the NH, its occurrence is after the seasonal

maximum in the SH. In the lower stratosphere, differences in HNO_3 vary both in magnitude and sign interannually and are more pronounced in the SH. This characteristic was also evident in the other ensemble members. Such year-to-year differences are only marginally seen in N_2O_5 .

[17] Figure 4 shows the climatological annual cycle of HNO_3 in both hemispheres, averaged poleward of 70° , for Aura/MLS (Figures 4a and 4b) based on monthly averages from the years 2004–2011, and for WACCM as an ensemble-mean based on monthly averages from 16 simulated years (Figures 4c and 4d: perturbed simulation, and Figures 4e and 4f: control simulation). The inclusion of the ion cluster reaction significantly improves the HNO_3 distribution throughout the year, especially in the SH (Figures 4b, 4d and 4f). The wintertime high-altitude abundance above 10 hPa, albeit improved, remains clearly lower than MLS, as the HNO_3 enhancements in WACCM do not extend as high as those measured by MLS or by SMR [e.g., Verronen *et al.*, 2011; Orsolini *et al.*, 2009]. In addition, the implementation of reaction (R1) has better aligned the model seasonal cycle with the observations above 10 hPa. In the NH (Figures 4a, 4c and 4e), the control simulation showed a warm season maximum, but the perturbed simulation now reveals a winter maximum, as observed by MLS. Below about 30 hPa however, HNO_3 is already overestimated in the control simulation compared to MLS, and the introduction of the pathway further increases this high bias. Although not included in the model, the MLS HNO_3 data also include the effects of solar proton events, e.g., in January 2005 (NH), September 2005 (SH), and December 2006 (NH).

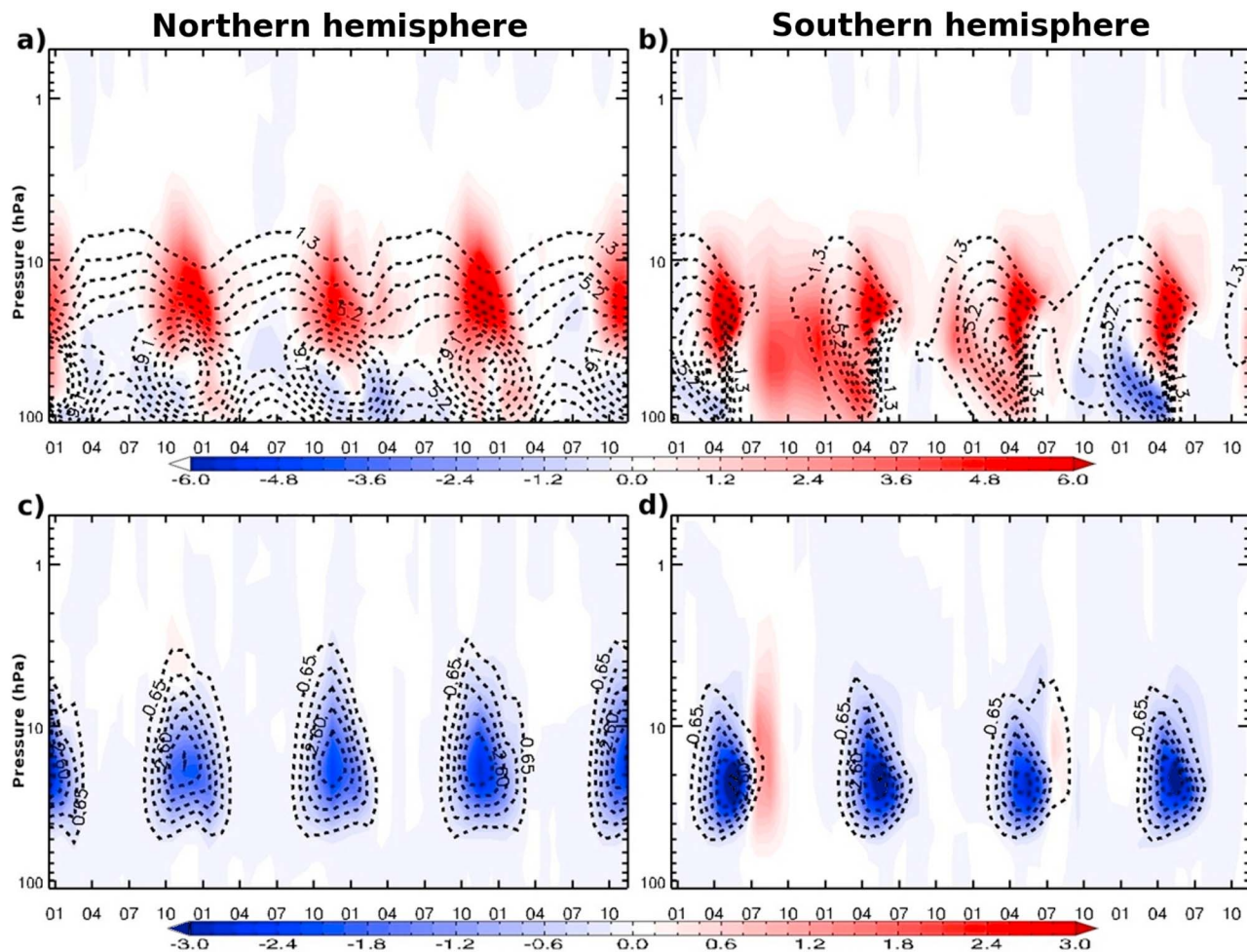


Figure 3. Time versus pressure evolution of the differences (perturbed minus control, color shaded) in (a, b) HNO_3 (in ppbv) and (c, d) N_2O_5 (in ppbv) for one ensemble member over the four simulated years (1999–2002), and averaged over polar regions (poleward of 70°) in the (left) northern and (right) southern hemispheres. Overlaid as dashed contour lines are the corresponding fields in the control simulation.

[18] The large occasional enhancements of HNO_3 in the lower stratosphere in the perturbed simulations, as in the first year in Figure 3b, can be explained by a spring break-up of the austral vortex. Such a break-up would lead to a poleward flux of HNO_3 from midlatitudes, where in fact HNO_3 is more abundant than at high latitudes [e.g., *Urban et al.*, 2009], due to permanent removal of HNO_3 by sedimentation of polar stratospheric cloud particles in winter. When the break-up occurs in late spring or summer, the meridional gradient of HNO_3 has waned, and it leaves a weak signature in HNO_3 . We will return in Section 4 to the issues of potential WACCM biases and the impact of our assumptions regarding the background ion cluster distribution. In that section, we will relate the lack of high-altitude HNO_3 formation to a lack of available N_2O_5 in WACCM, and the high HNO_3 bias in the lower stratosphere to an excessive winter descent.

3.2. Response in NO_x , N_2O and O_3

[19] The distributions of O_3 and NO_x are governed by chemistry as well as transport processes. The competition between these two processes differs in various regions and seasons, and we will use the ratio of NO_x/NO_y to separate

these processes. The difference in this ratio between the perturbed and the control simulations will deviate from zero (positively or negatively) if chemistry alters the NO_x abundance. Figure 5 shows the climatological annual cycle of the ensemble-mean difference between perturbed and control simulations, for NO_x , NO_x/NO_y -ratio and O_3 in the polar regions. The figure includes contours of statistical significance at the 0.9 and 0.75 levels. The corresponding ensemble-mean annual cycle from the control simulation is overlaid as dashed contours.

[20] We begin by describing the NO_x and NO_x/NO_y -ratio (Figures 5a–5d). Between approximately 5 and 50 hPa, the introduced re-partitioning within the nitrogen family induces a clear deficit in the NO_x/NO_y -ratio during the cold season when N_2O_5 is available and R1 is active. This is due to the fact that HNO_3 is a longer-lived reservoir for NO_x , and the regeneration of NO_x has slowed down. The polar-averaged deficit in NO_x/NO_y -ratio begins in the autumn in both hemispheres and is strongest during early and late winter - characteristics that are more salient in the SH.

[21] We infer that the NO_x positive anomalies in regions where the NO_x/NO_y -ratio difference is close to zero (e.g., in

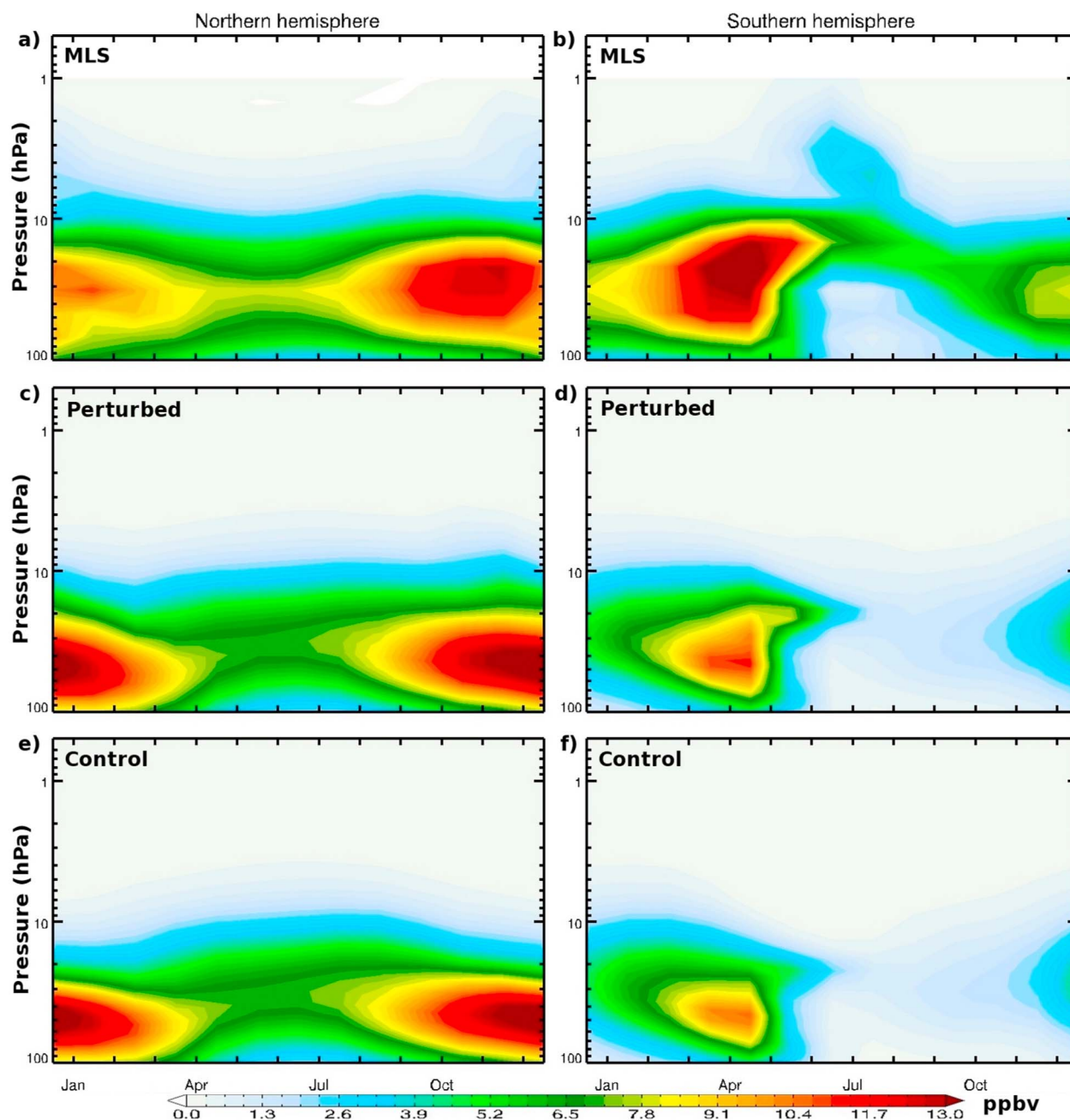


Figure 4. Climatological annual cycle of HNO_3 (ppbv) versus pressure, based on (a, b) monthly mean MLS data from 2004 to 2011, (c, d) ensemble mean from the WACCM perturbed simulation and (e, f) control simulation. Left and right columns show polar regions (poleward of 70°) in the northern and southern hemispheres, respectively.

the NH spring above 25 hPa, and in the SH winter, spring and summer above 50 hPa) are caused by transport and not by the direct influence of nitrogen chemistry. To further elucidate the origin of these anomalies, we examine in Figures 6a and 6b the climatological annual cycle of the ensemble-mean differences between the two simulations at 10 hPa as polar stereographic maps (40° – 90° N in Figure 6a, and 40° – 90° S in Figure 6b), for N_2O , NO_x , O_3 , and NO_x/NO_y -ratio. While Figure 6 shows every other month, the auxiliary material Figures S1a and S1b show the entire

seasonal cycle.¹ Ensemble-mean 10-hPa geopotential height differences are overlaid on the N_2O panels, while ensemble-mean geopotential height for the control and the perturbed simulations are shown on the O_3 and NO_x/NO_y panels, respectively. Figures 6a and 6b nicely show the annual cycle of the anomalies in NO_x (or in NO_x/NO_y), with a pronounced high-latitude deficit in the cold season. Polar,

¹Auxiliary material files are available in the HTML. doi:10.1029/2011JD017257.

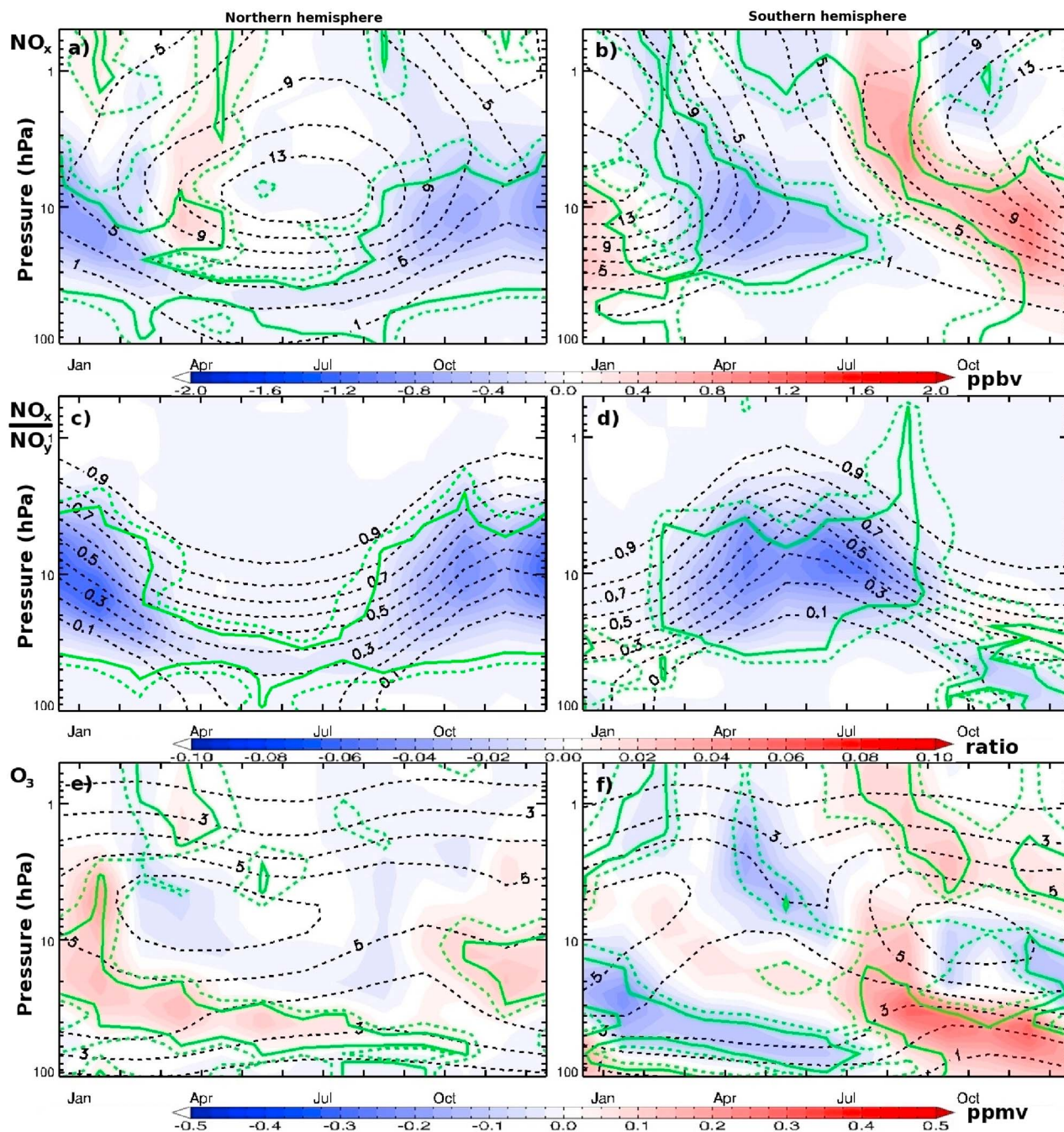


Figure 5. Climatological annual cycle of the ensemble mean differences (perturbed minus control, color shaded) in NO_x (ppbv), NO_x/NO_y ratio and O_3 (ppmv), averaged over polar regions (poleward of 70°) in the (a, c, e) northern and (b, d, f) southern hemispheres. Overlaid as dashed contour lines are the corresponding ensemble-mean fields in the control simulation. Significance at the 0.9 and 0.75 levels is indicated by the solid and dashed green contours, respectively.

positive N_2O anomalies are evident from late winter to summer in the SH, and in spring in the NH, correlated with anomalies in geopotential height. Such positive correlations between N_2O and geopotential height reflect the enhanced poleward transport from the N_2O -rich lower latitudes in a weakened polar vortex. As N_2O is photochemically converted into NO in the sunlit spring and summer, a concomitant increase in NO_x occurs. In the SH, the positive

anomalies in NO_x and N_2O are both stronger in magnitude and more prolonged, lasting well into the summer season (e.g., Figures 6a and 6b, first two rows).

[22] The perturbed run with its stronger poleward advection in spring and summer has in fact brought the WACCM annual climatological cycle of N_2O closer to MLS observations. This is demonstrated in Figure 7, which is the analogue of Figure 4 for N_2O . In the control simulation, in the

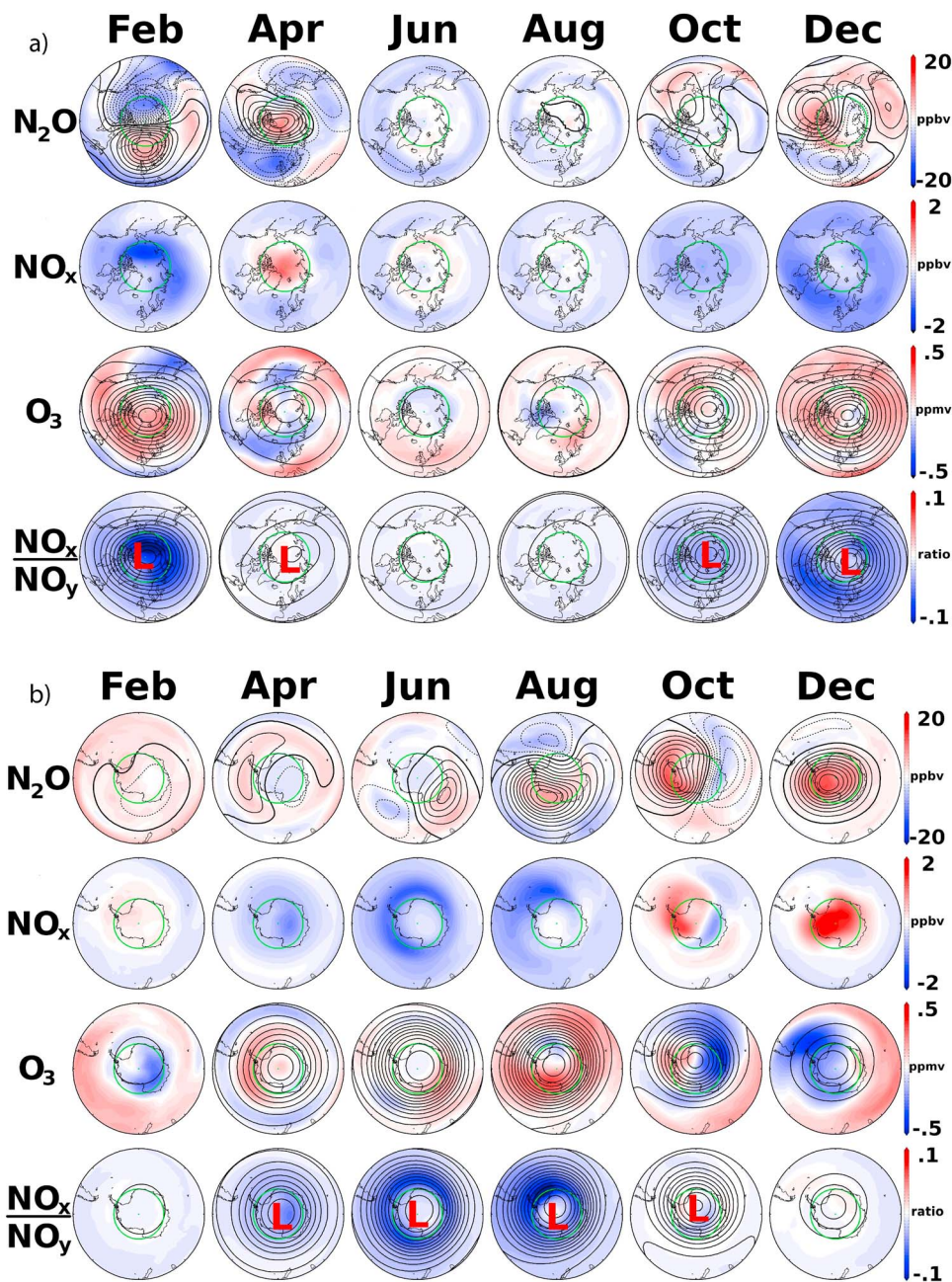


Figure 6. (a) Climatological annual cycle of the ensemble-mean difference (perturbed minus control, color shaded) for N_2O (ppbv), NO_x (ppbv), O_3 (ppmv) and the NO_x/NO_y -ratio at 10 hPa. Overlaid as black contour lines on N_2O maps are the corresponding ensemble-mean geopotential height differences, with dashed and solid being negative and positive values, respectively. Overlaid as black contour lines on O_3 and NO_x/NO_y -ratio maps are the corresponding ensemble-mean geopotential heights from the control and perturbed simulation, respectively. Contour interval is 160 m for geopotential height and 20 m for geopotential height differences. Capital L and H indicate Low (geopotential height minimum) and High (geopotential height maximum) from the perturbed simulation. Polar (40° – 90° N) stereographic maps, with green circle drawn at 70° N. (b) Same as in Figure 6a but for southern hemisphere (40° – 90° S). The contour intervals of geopotential height and geopotential height differences are 320 m and 40 m, respectively.

SH in particular, the late spring and summer polar abundances were too low and peaked too late compared to MLS. The perturbed run has higher abundances and a steeper seasonal increase, albeit still smaller than in the observations.

This is likely due to a tendency of this WACCM version to produce an austral polar vortex that is too long-lived, remaining climatologically strong until January (Figure 6b, third or fourth row). This would inhibit the poleward

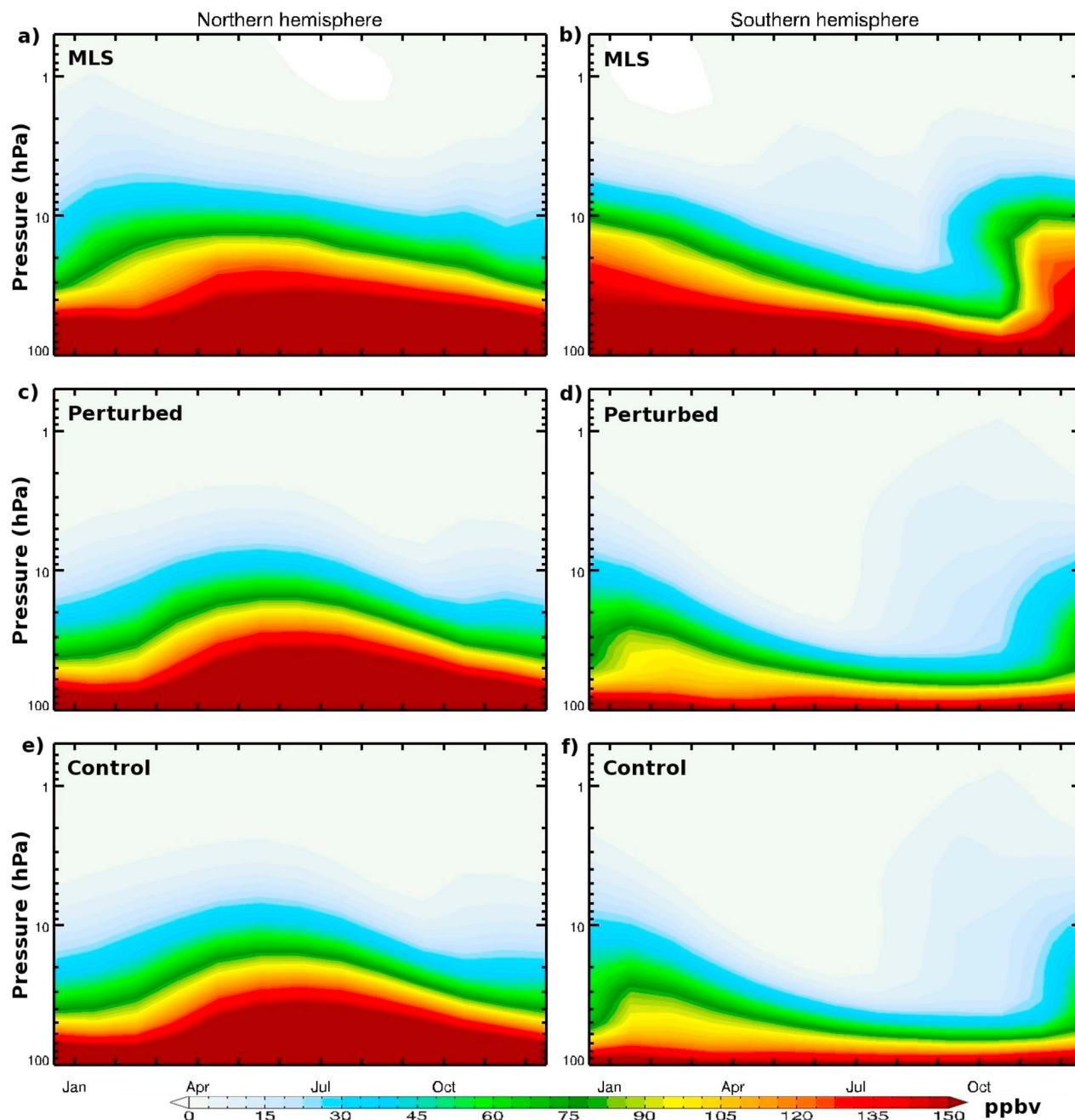


Figure 7. Climatological annual cycle of N_2O (ppbv) versus pressure, based on (a, b) monthly mean MLS data from 2004 to 2011, (c, d) ensemble mean from the WACCM perturbed simulation and (e, f) control simulation. Left and right columns show the polar regions (poleward of 70°) in the northern and southern hemispheres, respectively.

transport of N_2O rich air toward high latitudes. The earlier vortex weakening would also tend to alleviate the low N_2O bias in the control run. Because MLS data only covers the years 2004–2011, the observed higher abundances in the NH winter above 30 hPa could reflect the occurrences of several major stratospheric sudden warmings in years 2004, 2006, 2009 and 2010 [e.g., Orsolini et al., 2010; Manney et al., 2008], which would bring N_2O -rich air from lower latitudes poleward. The SSWs would not occur at the same frequency in these WACCM runs.

[23] In summary, in the perturbed case, a pattern of decreased NO_x abundance during winter is evident. The weaker spring vortex allows for a stronger poleward transport of N_2O , which translates into positive NO_x anomalies, stronger and longer lasting in the SH. The recurrent spring and summer NO_x excess in the mid-stratosphere is perhaps the most striking and unanticipated chemical anomaly arising from dynamical-chemical feedbacks, as it occurs when the cold-season ion cluster reaction (R1) is not active anymore.

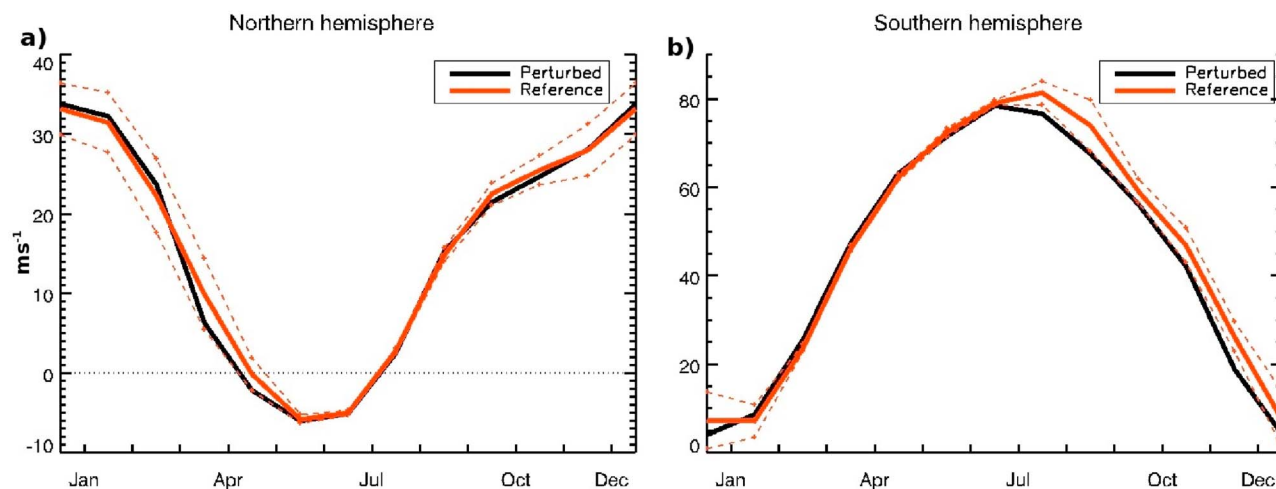


Figure 8. Climatological annual cycle of the monthly zonal-mean zonal wind at 10 hPa for the perturbed (black) and control (red) ensemble means, averaged over latitudes between (a) 60°–70° N and (b) 60°–70° S. The dashed red lines represent one standard deviation of the ensemble-mean control simulation.

[24] These altered NO_x levels have important consequences for the O_3 abundance. While the O_3 response is more complex, Figure 6 reveals strong positive anomalies in winter at mid and high latitudes, turning into weaker negative anomalies in the spring-summer (SH) or spring (NH). In both hemispheres, when sunlight returns to the polar regions in the spring, NO_x and O_3 are also clearly anti-correlated between the 30–5 hPa pressure range, where the NO_x catalytic cycle dominates (Figures 5a, 5b, 5e, and 5f). Below about 30 hPa, the O_3 increase is not accompanied by a negative anomaly in NO_x , but the change in the partitioning in NO_y implicated by the anomaly in the NO_x/NO_y ratio is indicative of a mitigating effect upon the halogen-induced O_3 depletion in this region.

3.3. Response in Zonal-Mean Winds and TEM Circulation

[25] The results above indicate that reaction (R1) leads to a weakened polar vortex during springtime. However, the origin of the zonal wind anomalies requires a careful analysis. This is further demonstrated in Figure 8, which shows the annual climatological cycle of zonal-mean zonal wind at 10 hPa averaged over the latitude band 60°–70°. The westerlies are weaker in the perturbed simulation during spring in the NH, and from winter to early summer in the SH. The zonal wind anomaly exceeds one standard deviation of the variability in the control simulation during July and November in the SH. These zonal wind decreases are not confined to the 10 hPa level, but rather extends throughout the entire stratosphere and lower mesosphere. This is demonstrated in Figure 9, which shows the monthly mean, ensemble-mean difference in zonally averaged zonal winds during the months where the zonal anomalies in Figure 8 are large, i.e., April–May in the NH and November–December in the SH. Overlaid are the corresponding zonal winds from the control simulation. In both hemispheres, these monthly mean negative wind anomalies are statistically significant, especially in late spring, at the 0.75 to 0.90 level depending on latitude or pressure. We now demonstrate that the weaker polar vortex in the perturbed run coexists with a stronger

planetary wave forcing diagnosed by the EPFD, and with a stronger TEM circulation. To this end, the ensemble-mean TEM circulation differences between the two simulations are diagnosed alongside the meridional distributions of the long-lived tracer N_2O . In Figures 10a, 10c, 10e and 10g, we present the climatological seasonal latitude-height distributions of the relative differences between the two simulations for N_2O (in percent and color shading). Note that small absolute differences in N_2O can appear as large relative differences. The corresponding N_2O distributions from the control simulation are overlaid as black contours. The corresponding TEM circulation is also overlaid as black vectors. The joint examination of the N_2O and TEM cross-sections further illustrates the polar enhancement in N_2O in the spring, as seen in the maps at 10 hPa (Figures 6a and 6b) and discussed in Section 3.2. In the SH, the enhancement started in winter and persisted during the summer season, before waning in the lower polar stratosphere, around 50 hPa, during the autumn season.

[26] Figures 10b, 10d, 10f and 10h show the difference in TEM circulation between the simulations, as vectors, as well as the difference in the EPFD in color shading. The largest differences in TEM are found in winter above 10 hPa, at midlatitudes in the NH and at mid or high latitudes in the SH. These differences correspond to a strengthening of the TEM circulation, which appears consistent with the negative (westward) anomaly in the EPFD. The strengthened circulation can only be attributed to forcing by planetary waves.

3.4. Link Between the O_3 and Dynamical Response

[27] The depth of the wind anomalies, extending throughout the stratosphere, the altitude of the largest incipient O_3 perturbations in autumn and early winter, near 10 hPa (Figure 5e) and the pronounced EPFD anomaly, all point toward amplification of planetary waves as being the lead factor.

[28] In winter, the NO_x catalytic cycle can be active up to sub-polar latitudes, giving rise to zonally asymmetric O_3 anomalies in response to opposite anomalies in NO_x (Figure 6). Recent work with chemistry-climate models has

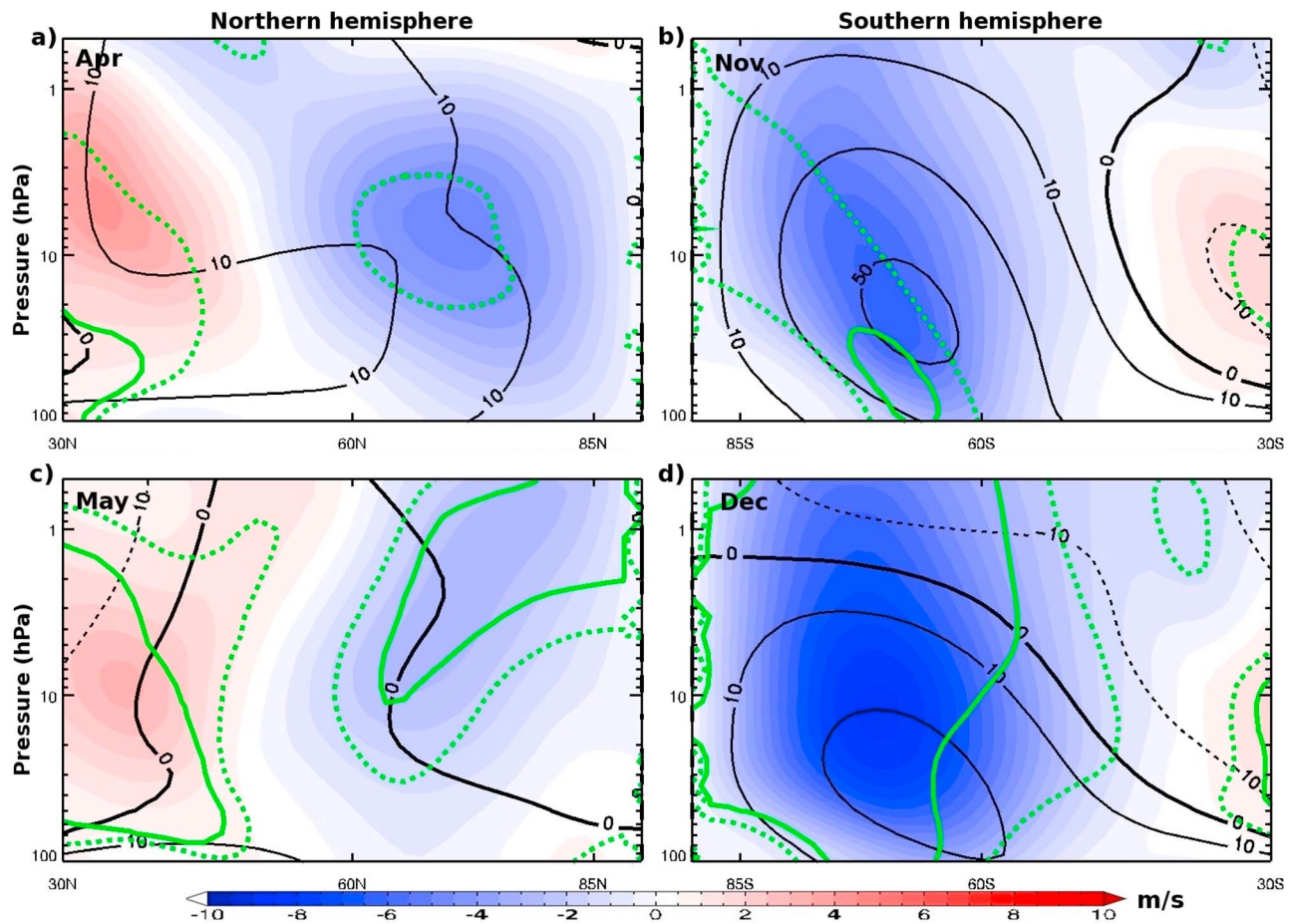


Figure 9. Monthly means ((a) April, (b) November, (c) May, (d) December) of the difference in the zonal-mean zonal wind as a function of latitude (30° – 90°) and pressure (perturbed minus control, color shaded). Overlaid is the zonal-mean zonal wind from the control simulation (black contours, negative values dashed and the zero line is thicker). Significance at the 0.75 and 0.9 levels is indicated by dashed and solid green contours, respectively.

demonstrated that using radiatively active O_3 tends to alter the generation and propagation of planetary waves, with a strong influence on the circulation throughout the stratosphere, compared to simulations where only zonally averaged O_3 is used radiatively [Kirchner and Peters, 2003; Gabriel et al., 2007; Gillett et al., 2009; Waugh et al., 2009; McCormack et al., 2011]. While we compare here two fully coupled simulations, the perturbed run has a higher degree of zonal asymmetry in O_3 . This is demonstrated in Figures 11a and 11b, which show the ensemble-mean climatological annual cycle of the standard deviation of ozone in the longitudinal direction at midlatitudes (30°S – 60°S or 30°N – 60°N), for the control simulation (dashed contours) and for the difference (perturbed minus control, color shading). In winter, the difference in the standard deviation is positive throughout the middle atmosphere in the SH, and above 10 hPa in the NH. This enhanced asymmetry in O_3 gives rise to short-wave heating anomalies, as demonstrated in Figures 11c and 11d at 10 hPa for the months of February (NH) and August (SH). The ozone ensemble-mean differences (color shading) are identical to those shown in Figure 6, but are shown here to be strongly correlated, as expected, to shortwave radiative heating rate anomalies, locally as high as 10%.

[29] It is not possible to fully disentangle the causality of the co-variability of planetary waves and O_3 resulting from multiple radiative-dynamical feedbacks between temperature and O_3 . Neither was it possible even in the simpler case of comparing runs with O_3 fully coupled to the radiation to runs with only zonally symmetric O_3 radiatively active in papers cited above. Nevertheless, our diagnostics support the argument that the enhanced zonal asymmetries in O_3 induced by the initial NO_x perturbations in winter middle and sub-polar latitudes would tend to amplify the planetary waves forcing leading to a strengthened TEM circulation, and a vortex that is significantly weakened earlier in the winter.

4. Further Discussion of Potential Biases in WACCM

[30] Sensitivity simulations with several different distributions of $\text{H}^+(\text{H}_2\text{O})_n$ have been completed (not shown), but failed to reproduce the polar HNO_3 enhancements reaching the stratopause, as observed in MLS (Figures 1 and 4) and SMR [Orsolini et al., 2009] data. This failure appears to be due to a low bias in the climatological distribution of N_2O_5 in the upper stratosphere in WACCM, and does not

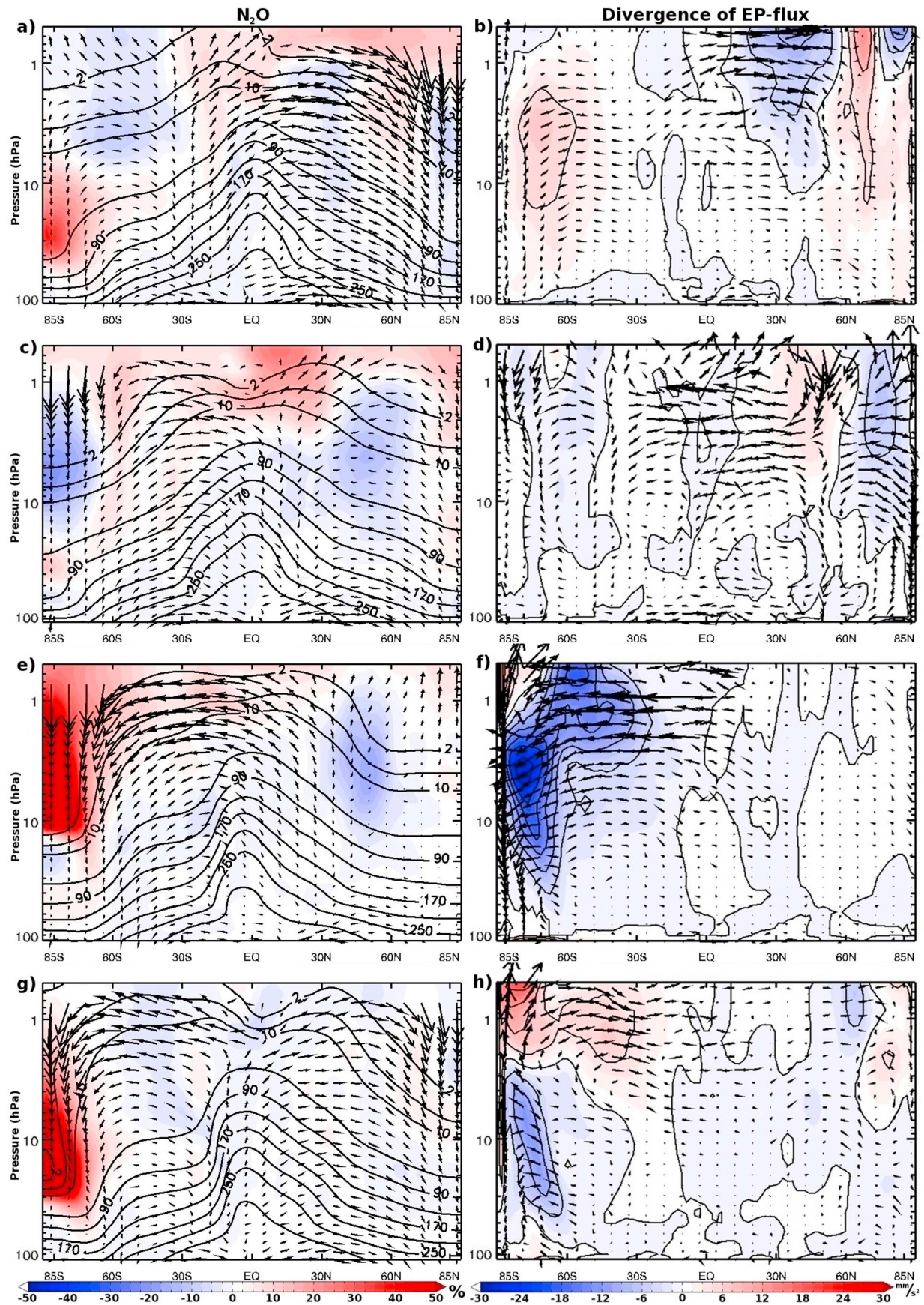


Figure 10

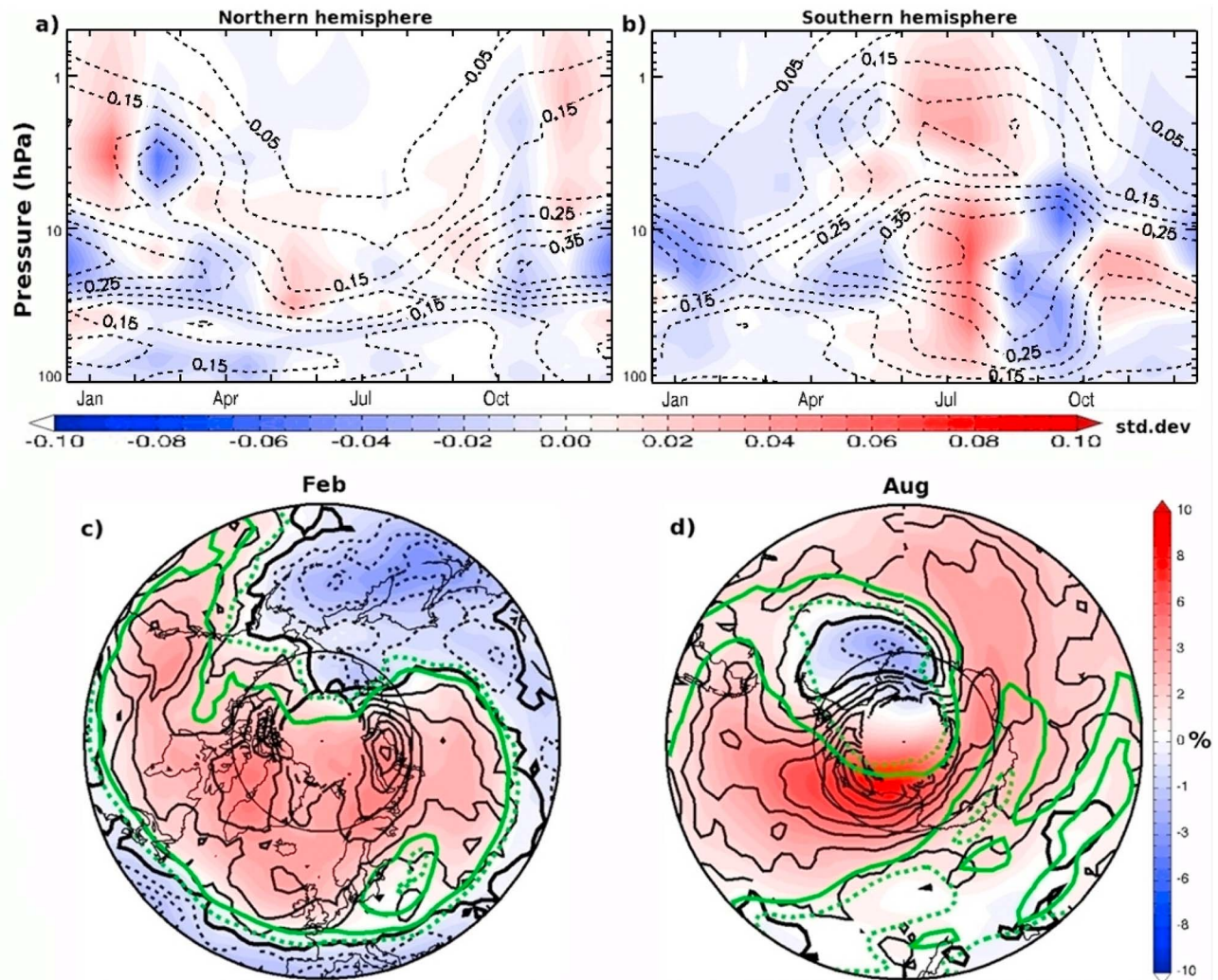


Figure 11. (a, b) Climatological annual cycle of the ensemble mean differences (perturbed minus control, color shaded) in the standard deviation for volume mixing ratio of O₃ (ppmv) in the longitudinal direction, averaged over the midlatitudes (30°–60°) in the northern and southern hemispheres. Overlaid as dashed contour lines are the corresponding fields in the ensemble-mean control simulation. (c, d) The climatological ensemble-mean relative difference (with respect to the control simulation, in % and color shaded) for O₃ at 10 hPa for February (NH) and August (SH). Overlaid as black contour lines are relative differences (in %) in the ensemble-mean shortwave radiative heating rates. Dashed and solid lines indicate negative and positive anomalies, respectively, with the zero line being thick; the contour interval is 1%. Significance at the 0.75 and 0.9 levels is indicated by dashed and solid green contours, respectively. The thin, solid, black circle is drawn at 70° in both hemispheres.

necessarily suggest that the observed HNO₃ enhancements originate from a different chemical processes. A comparison of the polar-averaged profile of N₂O₅ (>70° and DJF in the NH, >70° and MJJ in the SH) from both perturbed and control simulations together with MIPAS satellite observations is presented in Figure 12 (see Appendix A for more details

about MIPAS data). It reveals a low bias in WACCM in the upper stratosphere, above the levels where the HNO₃ perturbations in Figure 3 have decayed, i.e., 3 hPa in the NH, and 6 hPa in the SH. Hence, the potential for HNO₃ production in the upper stratosphere is insufficient due to a too low abundance of N₂O₅ in WACCM. In the upper

Figure 10. (a, c, e, g) Meridional distributions of the ensemble mean differences (perturbed minus control, color shaded, in percent) in N₂O for the DJF, MAM, JJA, and SON seasons. Overlaid as contour lines are the corresponding fields for the ensemble-mean control simulation, and as arrows is the TEM circulation also from the ensemble-mean control simulation. (b, d, f, h) Meridional distributions of the difference in the Eliassen-Palm flux divergence for the DJF, MAM, JJA, and SON seasons (color shaded). Overlaid as arrows is the difference in TEM circulation (perturbed minus control). Note that since the response in the TEM circulation is much smaller than the circulation itself, the vectors in the right column are not comparable in size to the vectors in the left column.

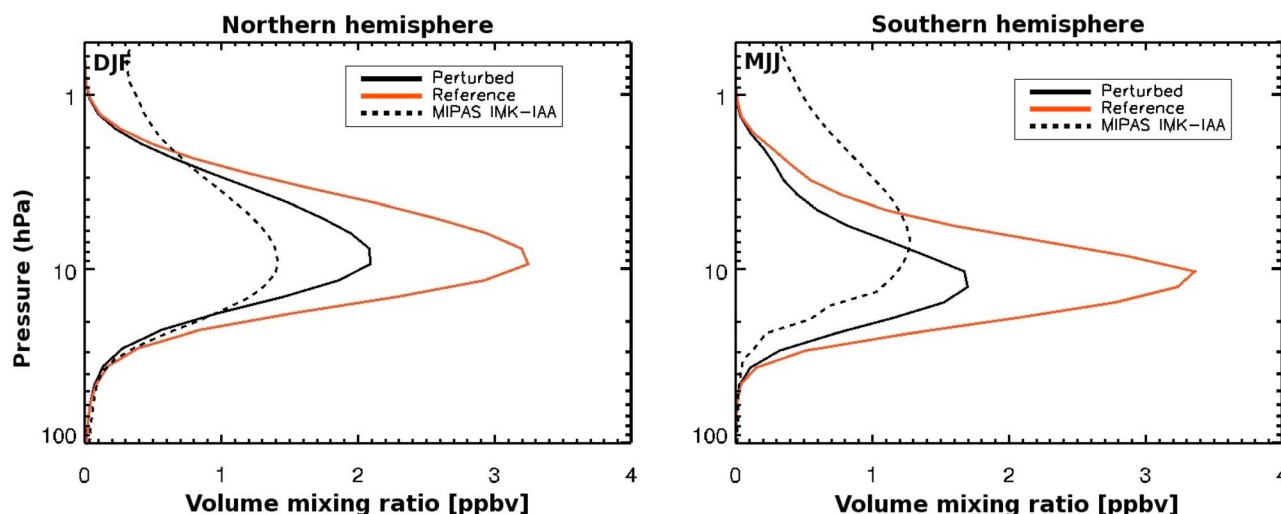


Figure 12. Vertical profiles of N_2O_5 (ppbv) for the DJF (NH) and MJJ (SH) seasons in the polar region (poleward of 70°) from the WACCM ensemble-mean perturbed simulation (solid black line), control simulation (solid red line) and MIPAS (dashed black line) data set (2007, 2008 and 2009).

stratosphere the use of an averaging kernel might help to reduce the differences between model and MIPAS observations. However, such a detailed comparison is beyond the scope of this study. Since the reaction that decomposes N_2O_5 is strongly dependent upon temperature, a warm model bias would cause the loss to be too large and hence a negative bias in N_2O_5 . A temperature comparison with MIPAS (not shown) indeed reveals a warm bias in the upper stratosphere in WACCM. We also surmise that the source of N_2O_5 , i.e., ultimately NO_x , is too low due to weak production from EPP or galactic cosmic rays. Another possibility is that the amount of NO_x descending into the stratosphere might be underestimated in WACCM because the elevated levels of NO_x created in the lower thermosphere do not reach the top of the descending branch of the TEM circulation [Smith *et al.*, 2011]. From the middle mesosphere down to the mid stratosphere, the TEM circulation is reasonably well captured in WACCM as demonstrated in the transport of carbon monoxide [Kvissel *et al.*, 2012]. Nevertheless, a further exploration of the causes of this upper stratospheric N_2O_5 deficit in WACCM is beyond the scope of this study. Below these levels, the high bias in the control run has been improved by the introduced N_2O_5 conversion through reaction (R1), and abundances of about 2 ppbv are closer to the MIPAS observations. In the middle stratosphere, the perturbed run still shows an excess of N_2O_5 that could be alleviated by a higher conversion rate to HNO_3 or a higher background abundance of hydrated ion clusters. We have chosen an idealized distribution of ion clusters, which is still poorly constrained by observations. The reaction rate k_2 and its potential dependence on cluster size could also be constrained by better experimental data.

[31] Another bias in these WACCM version 3.1.9 simulations concerns the anomalous persistence of the austral winter vortex into spring and early summer (e.g., Figures 8 or 9), which causes O_3 zonal anomalies in Figure 11 to be off phase with those in observations (Gillett *et al.*, 2009), and the downward TEM circulation in the lower stratosphere

to excessively compress and lower the N_2O contours (e.g., Figure 7).

5. Summary and Discussion

[32] In this paper, we have studied the WACCM response to the introduction of a chemical pathway that produces HNO_3 by conversion of N_2O_5 upon hydrated water clusters $\text{H}^+(\text{H}_2\text{O})_n$. The current study is the first of its kind, where this chemical reaction is introduced in a free-running CCM. As such, it is exploratory, and a time-independent distribution of hydrated water clusters has been prescribed in the model simulations. We aim to improve our understanding of the EPP- NO_x “indirect effect”; therefore, individual solar proton events are not included in the present study.

[33] We have used an ensemble approach, carrying out four pairs of control and perturbed simulations each lasting four years, and addressed the statistical significance of the results. The main focus has been on annually re-occurring chemical signatures in the polar regions. Despite the two model simulations being similar in all other aspects, it is not surprising that there are differences in the distributions of trace gases that can be attributed to changes in transport. The introduced chemical pathway for HNO_3 alters the internal partitioning of the NO_y family during winter months in both hemispheres, and the perturbed HNO_3 ultimately impacts the distribution of O_3 . Through O_3 changes, both temperature and dynamics are affected allowing for complex chemical-dynamical feedbacks lasting beyond the cold season when the reaction (R1) is active.

[34] Statistically significant changes in the climatological distributions of constituents from the nitrogen family or O_3 compared to the control run include: i) a cold season production and loss of HNO_3 and N_2O_5 , respectively, ii) a cold season decrease and increase in NO_x/NO_y ratio and O_3 , respectively, in the polar regions of both hemispheres, and iii) a NO_x and N_2O polar increase in spring-to-summer in the SH, and in spring in the NH. Associated with the later (iii) is an O_3 decrease, which is only statistically significant in the SH.

[35] Through the inclusion of the ion cluster reaction, we see an improved seasonal evolution of modeled HNO_3 compared to satellite observations from MLS, esp. regarding the seasonal cycle in the polar mid-stratosphere. However, a prior overestimation at lower levels in the NH is worsened by implementing reaction (R1). The N_2O distribution is also improved in the perturbed run compared to the MLS observations, esp. in the spring-to-summer in the SH. Our comparison of WACCM versus MLS observations also include O_3 , shown in auxiliary material Figure S2, but discrepancies in the lower stratosphere in winter and spring are difficult to ascribe to this effect only and not to other model processes, such as the anomalous vortex persistence or heterogeneous chemistry on PSCs.

[36] The seasonal evolution of zonal-mean zonal winds and temperature is not identical in the two simulations, which we argue is caused by strengthened planetary waves induced by the midlatitude zonal asymmetries in O_3 and short-wave heating. The strengthening in the perturbed runs ultimately results from the influence of the NO_x cold season deficit which leads to a higher degree of zonal asymmetry in O_3 at mid and sub-polar latitudes. In the SH, the weakening of the zonal-mean winds indeed begins in winter but is statistically most significant in late spring and summer, and in the NH, it is significant in the spring.

[37] The well-studied EPP- NO_x “indirect” effect allows O_3 depletion in the spring through the catalytic NO_x cycle [Jackman *et al.*, 2005, 2008; Randall *et al.*, 2006]. Our study uncovers a new way for the EPP- NO_x “indirect” effect to be further amplified in a model. The springtime polar NO_x increase arises from a weaker polar vortex that allows more transport of N_2O polewards, instead of in situ production of NO_x . On the other hand, the WACCM biases, e.g., in N_2O_5 , makes reaction (R1) ineffective above approximately 10 hPa, as shown in Figure 4. If WACCM would allow higher levels of NO_x to reach the stratosphere from above [Smith *et al.*, 2011], the EPP- NO_x “indirect” effect would yet be further amplified by the mechanism we propose here. As mentioned earlier, heterogeneous conversion of N_2O_5 into HNO_3 onto volcanic aerosols can also occur in the lower stratosphere [Bekki *et al.*, 1997], and the question arises whether analogous dynamical couplings would be at play when aerosol loading is large enough. The issues of N_2O_5 and dynamical biases in WACCM 3.1.9 make a compelling case for investigating the dynamical feedbacks of the reaction (R1) in other chemistry-climate models. Nevertheless, it is quite remarkable that the inclusion of this chemical pathway has changed the magnitude and the seasonal march of the stratospheric jet. Such change highlights the importance of NO_x in modulating ozone abundances, and of EPP processes for the entire middle atmosphere.

Appendix A

[38] In this study, we use the version 3.3 of Microwave Limb Sounder (MLS) L2 data. All the data were screened according to the instruction given in the MLS Data Quality and Description Document [Livesey *et al.*, 2011]. The MLS instrument is mounted on NASA Aura satellite, launched in 2004 into a sun-synchronous near-polar orbit. It measures the thermal emission of more than 15 trace species in the microwave range, in both day and night conditions, covering

latitudes up to 82° on each orbit. These measurements can be inverted into altitude profiles with a range between 215 and 0.01 hPa ($\approx 10\text{--}80$ km). The quality of the data varies considerably depending upon the height of the retrieval and the component retrieved. For HNO_3 , the standard recommended altitude range is between 215 and 1.5 hPa ($\approx 10\text{--}50$ km) [Livesey *et al.*, 2011, chapter 3.11]. The vertical resolution in the middle/upper stratosphere is 4–5 km up to about 1 hPa, where it starts to degrade rapidly down to 12 km around 0.1 hPa. Retrieved mixing ratios at 1 hPa are also scientifically useful during episodes when production of HNO_3 increases and the signal-to-noise ratio improves. These episodes can for instance happen during strong solar proton events [Verronen *et al.*, 2008, 2011], or during winters when an enhanced downward circulation advects NO_x -rich air from the mesosphere into the stratosphere.

[39] We have also used 3 years of N_2O_5 observations by MIPAS over the years 2007–2009. The MIPAS IMK-IAA data set from the Institute for Meteorology and Climate Research has been used (Atmospheric Trace Gases and Remote Sensing website: <http://www.imk-asf.kit.edu>). We have used the visibility flag and the averaging kernel (values less than 0.03 is removed) to remove bad data and data gaps.

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